Oxide ion conduction and dielectric relaxations for Ce$_{1-x}$Y$_x$O$_{2-x/2}$ system.

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Relationship between oxide ion conduction and dielectric relaxation in the Ce$_{1-x}$Y$_x$O$_{2-x/2}$ system ($0 \leq x \leq 0.5$) was investigated in order to clarify the dynamic properties of oxide ion conduction. The frequency dependence of dielectric constant was explained by the superposition of Debye-type polarization due to dopant-vacancy associates and charge current on electrolyte-electrode interface. The frequency dependence of ac conductivity was also explained by use of the dielectric parameters obtained from the numerical analysis of dielectric constant. Additionally, the polarization hysteresis curves of the oxide ion conductor were also measured to investigate the Debye-type dipoles in detail. As a result, it was found that the observed remanent polarizations have a close relation with the polarization of dopant-vacancy associates.

Key words: CeO$_2$, dielectric relaxation, fluorite type structure, oxide ion conduction

1. Introduction

Oxide ion conductors play an important role in such applications as oxygen sensors, oxygen pumps and solid oxide fuel cells (SOFCs) etc. Since SOFCs are required to decrease the operation temperature, high ionic conductivity is desired. Therefore, various materials having fluoride, perovskite and their related structures have been investigated. So far, the oxide ion conduction has been investigated by the dc four-probe and/or the ac impedance methods, and then the relationship between the crystal structure and activation energy for oxide ion conduction was discussed. As a result, many researchers suggest many factors for oxide ion conduction, for example, unit cell free volume, saddle point, ordering of oxygen vacancy and dopant-vacancy association etc. [1-3] However, the dominant factors for oxide ion conduction have not been clear.

The oxide ion conduction has a close relation with the electric dipole polarizations of oxygen vacancy. Our research group reported that the relationship between oxide ion conduction and dielectric relaxation from the viewpoints of dielectric constant, dielectric loss factor and loss tangent (tanδ) in the Sm, Nd, or Yb doped CeO$_2$ [4-6] and Y or Ca stabilized ZrO$_2$ [7,8] systems. According to those studies, the dielectric properties of oxide ion conductors can be explained by the superposition of Debye-type polarization due to the dopant-vacancy associates $[\text{Ln}_{c_1}$-$\text{V}_0]$ (Ln: dopant cation) and charge current on electrolyte-electrode interface. The dispersions of dielectric constant and electrical conductivity were ascribed to the Debye-type polarization. On the other hand, the dopant vacancy associates have been also reported by the mechanical loss spectra which show the internal friction [9, 10]. Additionally, the dielectric measurements for 8 mol% Y$_2$O$_3$ stabilized ZrO$_2$ were carried out in order to reveal the charge current, using platinum or oxide (La$_{0.6}$Ca$_{0.4}$MnO$_3$; LCMO) as different electrodes [11]. It was found that the two types of dopant-vacancy associates: dimer [Y$_2$-$\text{V}_0$] and trimer [Y$_{c_1}$-$\text{V}_0$-$Y_{c_2}$], which were observed for the platinum electrode, but these are decreased or disappeared for the LCMO electrode due to the incorporation of oxide ion from the oxide electrode into oxygen vacancy of electrolyte. Moreover, the dielectric relaxation measurement of 9 mol% Y$_2$O$_3$ doped ZrO$_2$ single crystal was carried out to explain the grain boundary effect [7].

In this study, we investigate the relationship for electrical conductivity, dielectric relaxation and polarization phenomena for Ce$_{1-x}$Y$_x$O$_{2-x/2}$ system ($0 \leq x \leq 0.5$) having a fluorite-type structure.

2. Experimental

Powder samples of Y-doped CeO$_2$ (Ce$_{1-x}$Y$_x$O$_{2-x/2}$) were prepared by solid state reaction, using CeO$_2$ (99.99 %, High Purity Chemicals, Japan) and Y$_2$O$_3$ (99.9 %, High Purity Chemicals, Japan) as starting materials. Weighed powders were wet ball-milled for 24 h using ethanol as dispersion reagent. The dried powder mixtures were calcined at 1273K for 10 h in air by using alumina crucible. After sieving with a mesh size of 53 µm, the powders were uniaxially pressed at 5 MPa and then rubber pressed at 200 MPa. Compacts thus obtained were sintered at 1873 K for 10 h in air, where the heating and cooling rates were 5 K/min. The relative densities of the sintered specimens, which were estimated from their geometrical dimensions.
and weight, were between 93.9 and 97.4 % of X-ray density. The powdered samples were characterized by X-ray diffraction (XRD) analysis (model: MultiFlex, Rigaku) with monochromated CuKα radiation. Lattice constant of the samples was estimated from XRD peaks by using the least squares method.

The dc electrical conductivity (σ<sub>dc</sub>) was measured by the dc four-probe method in the temperature range of 773 to 1173 K in air. Then dielectric constant (ε′) and dielectric loss factor (ε″) were obtained as a function of frequency by the two-probe method in the temperature range of 673 to 1173 K in air. The impedance analyzer (4129A LF, Yokogawa-Hewlett-Packard, Japan) was used for the dielectric measurement in the frequency range of 5 Hz to 13 MHz. Kaleida Graph (Synergy Software) was used for the numerical analysis of dielectric properties. Additionally, the polarization measurements (Precision LC, Precision 4 kV HIV, and High Voltage Amplifier, RADIANT) were also carried out to clarify the Debye-type polarization in the temperature range of 323 to 473 K.

3. Results and discussion

The XRD experiments revealed that the Ce<sub>1-x</sub>Y<sub>x</sub>O<sub>2-x/2</sub> system was a single cubic phase of the fluorite-type structure in the composition range of 0 ≤ x ≤ 0.3. However, the specimens in the range of 0.4 ≤ x ≤ 0.5 were assigned to a rare earth C-type structure on a basis of superstructure lines in the XRD patterns. Figure 1 shows the lattice constant as a function of the composition (x) in the Ce<sub>1-x</sub>Y<sub>x</sub>O<sub>2-x/2</sub> system. The lattice constant decreased nonlinearly with increase of the Y content. The calculated values of lattice constant were obtained from a following equation which was reported by Hong and Virkar [12].

\[
\alpha_{cal} = \frac{4}{\sqrt{3}} \left[ x r_Y + (1 - x) r_{Ce} + (1 - 0.25x) r_O + 0.25x r_{Ov} \right] \times 0.9971, \tag{1}
\]

where \( r_Y, r_{Ce}, r_O \) and \( r_{Ov} \) are the ionic radii of Y<sup>3+</sup> (0.1019 nm in 8 coordination and 0.096 nm in 7 one), Ce<sup>4+</sup> (0.097 nm in 8 coordination), oxide ion (0.138 nm) and oxygen vacancy (0.1164 nm), respectively, and 0.9971 is a multiplication factor in order to fit the calculated value for the observed value of pure CeO<sub>2</sub>. The calculation of the lattice constant was carried out according to following two types of models. In the model A, Y<sup>3+</sup> ion and Ce<sup>4+</sup> ion are coordinated by 8 by oxygen ions. In the model B, Ce<sup>4+</sup> ion is coordinated by 8 oxygen ions, but the half amount of Y<sup>3+</sup> ion is coordinated by 7 oxygen ions. The model B is based on the literature which reported by Maekawa et al. [13]. When the composition (x) increased, the lattice constant approached to the value of model B. Therefore, it is supposed that Y<sup>3+</sup> ion changes to 7 coordination with increasing composition (x).

Figure 2 shows a compositional dependence of σ<sub>dc</sub> at various temperatures for the Ce<sub>1-x</sub>Y<sub>x</sub>O<sub>2-x/2</sub> system. The electrical conductivity increased with increasing composition (x) in the range of 0 ≤ x ≤ 0.2, and then decreased with increasing composition (x) in the range of 0.2 ≤ x ≤ 0.5. This result agreed with that of the Nd or Sm doped CeO<sub>2</sub> systems. The decrease of the conductivity in the range of 0.2 ≤ x ≤ 0.5 would be ascribed to an ordering of oxygen vacancy.

Figure 3 shows a frequency dependence of dielectric constant (ε′) for the sample with x = 0.2 having the highest conductivity. The dielectric constant of oxide ion conductor was consisted of both the Debye-type polarization due to the dopant-vacancy associates and charge current on electrolyte-electrode interface. The large dispersions were observed at various temperatures.
Figure 4 shows a typical example of numerical analysis of dielectric constant for the sample with \( x = 0.2 \) at 973 K, which can be given by the following eq. (2)

\[
\varepsilon_r = \varepsilon_r^\prime + \frac{\varepsilon_r^\prime \cdot \varepsilon_r^\prime(0)}{1 + (\omega \tau_1)^2} + \varepsilon_r(0) \frac{1}{\omega^s},
\]

where the second term of right side corresponds to Debye-type polarization and the third term is charge current on electrolyte-electrode interface. The \( \varepsilon_r^\prime \) and \( \tau_1 \) represent the dielectric constant at the low frequency limit due to the \( i \)-th Debye-type polarization and the \( i \)-th dipole relaxation time, respectively. The \( \varepsilon_r^\prime(0) \) represents the dielectric constant at the high frequency limit. The \( \varepsilon_r(0) \) is defined as the dielectric constant due to the absorption current at the low frequency limit. The exponent \( (s) \) is introduced to generalize the equation as the function of frequency. Two Debye-type dipoles were observed in the temperature range of 773 to 1173 K. The third Debye-type dipole was observed in 673 K. These dipoles were named Dipole 1, 2, and 3 in order of increasing frequency: therefore, the dielectric constants and relaxation times of the Debye-type dipoles were denoted as \( \varepsilon_r^\prime(0) \), \( \varepsilon_r^\prime \), and \( \tau_1 \), \( \tau_2 \) and \( \tau_3 \), respectively. These dielectric parameters obtained from the numerical analysis are summarized in Table 1.

Our research group has reported that the two kinds of dipole polarizations were observed in 9 mol\% \( Y_2O_3 \) stabilized \( ZrO_2 \) which correspond to dopant-vacancy associates; dimer type \([Y\ Zr^{\prime\prime\prime} - V_{O^{\prime\prime\prime}}]\) and trimer type \([Y\ Zr^{\prime\prime\prime} - V_{O^{\prime\prime\prime}} - Y\ Zr^{\prime\prime\prime}]\) [11]. In this study, therefore, Dipole 2 and 3 correspond to \([Y\ Ce^{\prime\prime\prime} - V_{O^{\prime\prime\prime}}]\) and \([Y\ Ce^{\prime\prime\prime} - V_{O^{\prime\prime\prime}} - Y\ Ce^{\prime\prime\prime}]\), respectively. Dipole 1 which appeared in the high frequency region at the 673 K corresponds to long range migration of oxygen vacancy. The activation energy of relaxation frequency (inverse of \( \tau_1 \)) could be estimated using the Arrhenius equation. The relation between activation energy estimated from relaxation frequency and electrical conductivity was discussed in our other published paper [6].

Figure 5 shows a frequency dependence of \( \sigma_{ac} \) for the sample with \( x = 0.2 \) in the temperature of 673 to 1173 K, where the large dispersion was observed. In order to understand the frequency dependence of \( \sigma_{ac} \), the numerical analysis was carried out using following eq. (3).

\[
\sigma_{ac} = \omega \varepsilon_0 \varepsilon_r'' = \sigma(0) + \omega \varepsilon_0 \left( \sum_{i} \varepsilon_r'' \frac{\varepsilon_r(0)}{1 + (\omega \tau_i)^2} \right) \varepsilon_r(0) \frac{1}{\omega^s}
\]

where only \( \sigma(0) \) must be estimated from the numerical analysis of dielectric loss factor (\( \varepsilon_r'' \)), using following eq. (4).

\[
\varepsilon_r'' = \sum_{i} \varepsilon_r'' \frac{\varepsilon_r(0)}{1 + (\omega \tau_i)^2} + \frac{\varepsilon_r''}{\omega^s}
\]

The calculation values for frequency dependence of \( \sigma_{ac} \) are also shown as solid lines in Fig. 5. As the results, the calculated values of \( \sigma_{ac} \) agreed well with the observed values. This fact suggests that the large dispersion of \( \sigma_{ac} \) was caused by the relaxations of Debye-type dipoles.

Noguchi et al. [14] reported that the association pair composing of oxygen vacancy and A-site vacancy in ferroelectricity of Bi\(_0.5\)Na\(_0.5\)TiO\(_3\) based single crystal affects the ferroelectric properties. Therefore, the polarization measurement was carried out to investigate the dopant-vacancy associates in detail. Figure 6 shows a typical example of polarization hysteresis curve for the sample with \( x = 0.2 \) at 399 K. The remanent polarizations \( (P_r) \) increased with increase of temperatures, suggesting thermal activation process. The dielectric constant can be calculated by the following eqs. (5) and (6) using the \( P_r \) values,

\[
P_r = \frac{Q}{A} C \times \frac{V}{A}, \quad \varepsilon_r'' = \frac{dC}{\varepsilon_0 A}, \quad \varepsilon_r'' = \frac{\varepsilon_r''}{\varepsilon_0 A}
\]

where \( Q, C \) and \( V \) are the electrical charge, the electrical capacity and the applied voltage, respectively. The \( A \) and \( d \) represent the area and the thickness of the sample.
Oxide ion conduction and dielectric relaxations for Ce₃₋ₓYₓO₂₋x/2 system

Table 1 Dielectric parameters of Ce₀.8Y₀.2O₁.9.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>ε₀₁</th>
<th>ε₀₂</th>
<th>ε₀₃</th>
<th>τ₁ (s)</th>
<th>τ₂ (s)</th>
<th>τ₃ (s)</th>
<th>ε₀(0)</th>
<th>s</th>
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<tr>
<td>1173</td>
<td>8.14×10⁵</td>
<td>4.07×10⁶</td>
<td>1.87×10⁷</td>
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Hereafter, the dielectric constant obtained from the dielectric measurement is written as ε₀(d) and that obtained from the polarization measurement is ε₀(p).

Figure 7 shows the Arrhenius plots of ε₀(p), which changed linearly. ε₀(p) showed the maximum value in the composition range between x = 0.05 and x = 0.1.

Fig.6 Polarization hysteresis curve for x = 0.2 at 399K.

Fig.7 Arrhenius plots of dielectric constant for Ce₀.8Y₀.2O₁.9 system (calculated by remanent hysteresis).

Fig.8 The activation energy (estimated by Fig.7) as a function of composition (x).

Fig.9 Arrhenius plot of dielectric constant for the sample with x = 0.2 (measured by each measurements)

The Pᵣ value decreased with increasing composition (x) in the range of 0.1 < x < 0.3, and almost disappeared below 473 K for the samples with x = 0.4 and 0.5. If the temperature increases above 473 K, the Pᵣ will be appeared. The composition dependence of activation energy estimated from ε₀(p) is shown in Fig.8. The activation energy increased linearly with increasing
composition ($x$). It suggests that this activation energy may correspond to the reorientation of Debye-type dipoles due to the dopant-vacancy associates. Finally, Fig. 9 shows the comparison of $\varepsilon_{r(d)}$ and $\varepsilon_{r(p)}$ in order to clarify the relationship of the two kinds of polarizations for the sample with $x = 0.2$. The $\varepsilon_{r(d)}$ includes the two Debye-type dipoles as Dipole 2 and 3 due to the dopant-vacancy associates. As seen in Fig. 9, since the $\varepsilon_{r(d)}$ agreed well with the $\varepsilon_{r(p)}$ in the Arrhenius relation, it was revealed that each dielectric constant was originated from the same phenomenon.

4. Conclusion

The dc electrical conductivity of the Ce$_{1-x}$Y$_x$O$_{2-x/2}$ system showed the highest value at $x = 0.2$. The numerical analysis of frequency dependence of dielectric constant ($\varepsilon_r'$) was explained by the superposition of Debye-type polarization due to the dopant-vacancy associates and charge current on electrolyte-electrode interface. The three Debye-type polarizations were observed. The Debye 1 which appeared in the highest frequency at 673 K was ascribed to the long range migration of oxygen vacancy, and the other two polarizations in the lower frequencies originated from the dopant-vacancy associates [Y Ce′-VO ‧‧ and \[Y Ce′-VO ‧‧-YCe′\]]. The remanent polarization ($P_r$) was observed in the present oxide ion conductors, and the activation energy estimated from $\varepsilon_{r(p)}$ may correspond to the reorientation of Debye-type dipoles due to the dopant-vacancy associates.

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References